5p

X63-11358

NASA TT F-8299

Code 2D

MEASUREMENT OF THE POTENTIAL OF A CATALYST IN THE COURSE OF REACTION. USE OF "DISPERSED" ELECTRODES

by P. Boutry, O. Bloch, and J. C. Balaceanu

FACILITY FORM 602

N71-71144 (ACCESSION NUMBER)

5 (PAGES)

✓ (NASA CR OR TMX OR AD NUMBER)

(THRU) Non (CODE)

(CATEGORY)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON February 1963

MEASUREMENT OF THE POTENTIAL OF A CATALYST IN THE COURSE OF REACTION. USE OF "DISPERSED" ELECTRODES

Note[1] by Pierre Boutry, Odile Bloch and
Jean-Claude Balaceanu, presented by Paul Pascal.

It is shown that a catalyst in suspension in an electrolyte, in the presence of a collector conductor, constitutes an electrode that presents all the properties and uses of classic compact electrodes. Such a device permits among other things the following of the potential of the catalyst in the course of a reaction.

Within the framework of a study of catalytic reductions of multivalent mineral ions by hydrogen in the aqueous phase, we undertook the measurement and interpretation of the variation of potential assumed by the catalyst dispersed in the solution in the course of the reaction, using a technique analogous to that of Sokolsky et al. (Ref. 1)

A rapid and important method of studying the electrochemical behavior of a substance on an electrode consists in constructing its polarization curve (Ref. 2). This curve, which is specific for the combination, substance + electrode, makes it possible to compare various electrodes by using an identical substance. We thus constructed characteristic curves for hydrogen in an acid medium (H_2SO_4 5 N) with various electrodes using the cell of the diagram in Figure 1. The reference electrode utilized was a mercurous sulfate electrode with a saturated K_2SO_4 bridge. The potential was set at $\pm$ 5 mV by means of a Tacussel potentiostat (PRT 2000). The solution, thermostatically controlled for 30° C, was stirred by a magnetized bar driven by a magnetic agitator.

We first verified that this potential was the function of the catalyst only, by studying the behavior of an electrode formed by a wire or by a polished metal plate immersed in a suspension of a catalyst consisting of platinum on carbon (5 percent Pt), as compared to a platinized platinum electrode with the same dimensions.

The various metals used were: Au (wire), W (wire), Pt (wire and plate), Cu (wire). All these metals with the exception of copper are unalterable in our solutions. As to copper, when the electrode thus constituted is immersed into the acid solution in the absence of the

[1] Meeting of 19 March 1962

Typed by _____ Corrections proofread by _____
Proofread by JS Corrections put in by _____
Corrections typed by _____ Final check by _____

catalyst, it assumes the potential corresponding to the dissolution of copper even in a hydrogen atmosphere. On the other hand, if the catalyst is added under the same conditions, the obtained potential corresponds to the equilibrium $H_2 \rightleftharpoons 2H^+ + 2e$ on platinum. The hydrogen polarization curve can be constructed for the other metals with the catalyst present. These curves are identical when without catalyst the oxidation of hydrogen is impossible (Au, W) or very weak (polished Pt).

The electrochemical properties of the "dispersed" electrode consisting of the catalyst in suspension and the wire or polished metal plate (which we call the "collector") are thus characteristic of the catalyst and independent of the nature of the collector. /2584

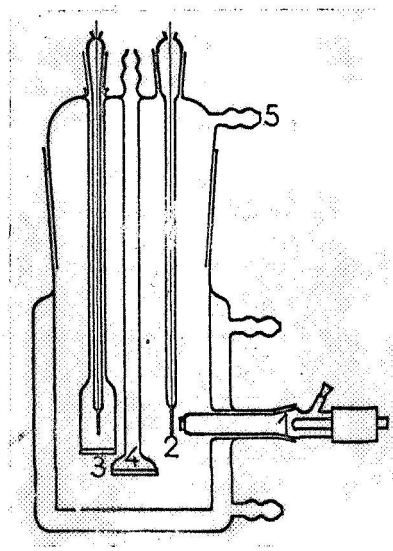


Figure 1. Electrolysis cell. 1, reference electrode; 2, indicator electrode; 3, counter electrode; 4, gas inlet; 5, gas outlet.

This point established, the effect of the mass of the catalyst suspended in the electrolytic solution was studied with regard to the resulting intensity, under a condition of constant agitation. To this end we constructed the polarization curve of hydrogen on a plate of polished platinum (1 x 1 x 0.5 cm) first alone, then in the presence of increasing quantities of catalyst. We then covered the same plate with a deposit of platinum black and constructed the polarization curve.

Typed by _____ Corrections proofread by _____
Proofread by J. _____ Corrections cut in by _____
Corrections typed by _____ Final check by _____

The results obtained (Figure 2) show that the solution saturates and that the resulting intensity reaches a limit close to that obtained with platinized platinum. One may therefore assume that for appreciable quantities of catalyst the limiting factor is traceable to the geometric dimensions of the collector.

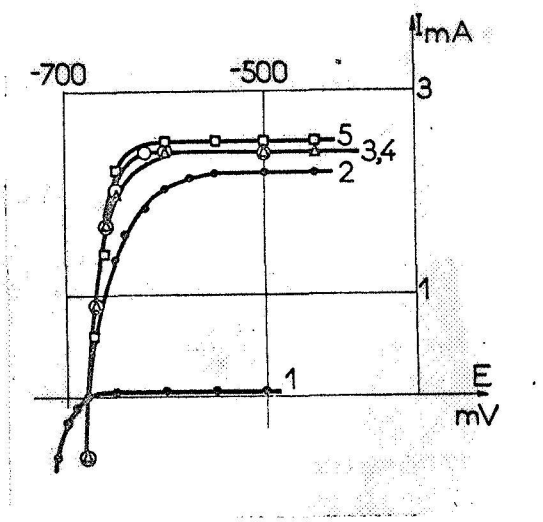


Figure 2. Polarization curves for hydrogen.

The "dispersed" electrode has thus the same characteristics as a compact electrode of the same dimensions as the collector, and these electrodes have identical electrochemical behavior.

Consequently it appears possible to apply to dispersed electrodes the various electrochemical considerations relating to compact electrodes and thus to gain by inference a certain amount of information about the activity of the catalyst itself or concerning compounds that may be found on the surface of this catalyst.

It is thus possible to trace the polarization curves for a given reactant on dispersed electrodes consisting of identical quantities of various catalysts and to compare the obtained current densities: the greatest densities will correspond to the most active catalysts. In studying the activity of a gram of platinum, we have thus been able to see that platinum on used carbon (5 percent Pt) was 1.3 times more active than Degussa colloidal platinum (1 percent Pt) for the reduction of mineral ions. /2585

Given a reactant in an adsorbed state on a powdered catalyst, it would appear possible to determine the total quantity of the adsorbed reactant by application of chronopotentiometric and chronoamperometric

Typed by _____ Corrections proofread by _____
Proofread by JS Corrections cut in by _____
Corrections typed by _____ Final check by _____

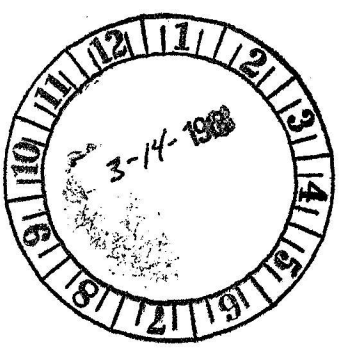
methods to this type of electrode. It is also possible, as demonstrated by Shlygin and Podvyazkin (Ref. 3) to determine the surface of the catalyst. Precautions must be taken in any case in a study of this kind because it is not possible to set a potential on the whole of the catalyst in suspension, but only on the fraction that at any given instant is in contact with the collector.

On the other hand, the potential assumed by the catalyst in the presence of mixtures of various oxidizing or reducing reactants is a mixed potential with a value corresponding to the uniformity of speeds of oxidation and reduction, the catalyst grains being in open circuit (Ref. 4). This makes it possible, by combining electrochemical and kinetic measurements, to study a certain number of reactions in an ionizing medium.

REFERENCES

1. Sokolsky, D. V., and Druz, V. A. Doklady Akad. Nauk. SSSR, 73, 1950, p. 949; Zhur. Fiz. Khim., 26, 1952, p. 364 (Chem. Abst., 1952, p. 4715 f); Y. A. Skopin and D. V. Sokolsky, Vestnik Akad. Nauk. Kazakh SSR, 12, no 6, 1956, p. 89 (Chem. Abst., 1956, p. 14471 b); D. V. Sokolsky and G. D. Zakymbaeva, Proc. Acad. Sc. URSS, 124, 1959, p. 153; D. V. Sokolsky and V. P. Chmonina, Actes 2e Cong. Intern. Catalyse, 2, Technip, Paris, 1961, p. 2733.
2. Charlot, G., Badoz-Lambling, J., and Tremillon, B. Les réactions électrochimiques (Electrochemical reactions). Paris, Masson, 1959.
3. Podvyazkin, Yu A., and Shlygin, A. I. Soviet Electrochemistry, I, Consultants bureau, New York, 1961, p. 27.
4. Boutry, P., Bloch, O., and Balaceanu, J. C. Bull. Soc. Chim. Fr. (in press).

Typed by _____ Corrections proofread by _____
Proofread by _____ Corrections cut in by _____
Corrections typed by _____ Final check by _____


3-14-1988